Journal of Applied Packaging Research

Volume 8
Number 4 *Special Issue of API 2015-Part 2*

Article 1

2016

Improving the Process Ability of Poly (3-Hydroxybutyrate) By A Polyphenolic Natural Additive

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RESEARCH ARTICLE

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ABSTRACT

The severe environmental issues generated by the non-biodegradability of most polymeric materials has fostered the search for more eco-friendly solutions. Polyhydroxybutyrate (PHB), produced by bacterial cells and easily hydrolyzed is one of appealing choice but its properties are still not competitive with those of standard polymers. Among others, one reason is related to the fact that the high processing temperature (due to the high crystallization point) is responsible for severe thermal degradation. In this paper, the effect of Tannic Acid (TA) as a thermal stabilizing processing agent for HPB is investigated by rheological as well as calorimetric techniques under conditions similar to those used in real processing applications. The results show that TA is effective in improving the thermal stability and processability of PHB, while keeping its biodegradable attitude. Compared to neat PHB, TA containing samples show a lower and delayed thermal degradation. FTIR measurements support the hypothesis that stabilization is determined by TA/PHB crosslinking.

1.0 INTRODUCTION

The severe environmental issues generated by the non-biodegradability of most polymeric materials has fostered the search for more eco-friendly solutions. Biodegradable plastics are polymeric materials that completely decompose by natural processes in a relatively short time, thus reducing the negative impact on health and environment [1,2].

Polyhydroxybutyrate (PHB), produced by bacterial cells and easily hydrolyzed [3] is one of the most studied biodegradable polymers. Although promising, its properties are still poorer than those of standard polymers. On the one hand, the high crystallinity makes PHB a very brittle and fragile material. On the other hand, the high crystallization temperature requires high processing temperatures, thus determining thermal degradation. [4]. For these reasons, PHB is always processed by adding different types of property modifiers, such as antioxidants, plasticizers, thermal stabilizers, processing aids [5,6].

In order to keep the full bio-degradability of the system, natural additives would be highly desirable. Within the category of antioxidants tannic acid, a commercial form of tannin and a strong antioxidant, can be extracted from plants and vegetable products including, for example, the grape residues from the wine industry [7,8]. Use of tannic acid as a thermal stabilizer for PHB, therefore, represents a promising route for preserving the complete bio-degradability of the polymer while improving its processing and use performance.

Aim of this paper is to study the effect of tannic acid on the processing stability of PHB. A commercial, purified form of tannic acid is added to commercial PHB samples and the thermal stability of these model systems is studied by rheological as well as calorimetric techniques under conditions similar to those used in real processing applications.

2.0 EXPERIMENTAL

2.1 Materials

The Polyhydroxybutyrate (PHB) used in this work has been kindly provided by Biomer (Germany), under the code T19, in powder form. The weight average molecular weight, Mw, as determined by gel permeation chromatography, is 890 kDa. The naturally extracted tannic acid (TA) supplied by Sigma-Aldrich (Italy) has been used, with an average molecular weight of 1701 Da.

Both PHB and TA have been used as provided. PHB/TA compounds have been prepared by adding vacuum oven dried TA and PHB to methanol. Solvent evaporation from the resulting suspension has been helped by mechanical agitation at 50°C and subsequent vacuum oven treatment at 60°C for 24 h. Samples were then milled to powder. Three weight fractions of tannic acid were used, 5%, 10% and 15%, respectively and referred to as PHB/TA5, PHB/TA10 and PHB/TA15

2.2 Experimental Methods

Rheological measurements were carried out on a stress controlled rheometer (Rheometrics SR 200, Inc., USA) equipped with 25 mm diameter parallel plates and a gap size of 1 mm. Temperature stability was guaranteed by a conductive/radiating electrical oven system fed by a nitrogen atmosphere to minimizing degradation.

Differential Scanning Calorimetry (DSC) measurements were performed by a Shimadzu 60 instrument (Shimadzu Corporation, Japan) under nitrogen atmosphere. The scanning rate was in all cases 10°C/min.

Thermogravimetric Analysis (TGA) was carried out on a Perkin Elmer Pyris Diamond TG-DTA instrument under nitrogen atmosphere. in the temperature range 20-600°C with a heating rate of 20°C/min.

FTIR-ATR spectroscopy was carried out on molten samples simultaneously to rheological tests by means of a Rheonaut ATR sampling module coupled to a Thermo Scientific HAAKE MARS III rheometer. Spectra were recorded as an average of 32 scans in the range 4000-400 cm-1, with a resolution of 4 cm-1. Prior to measurements, the samples were kept overnight at 60 °C under vacuum.

3.0 RESULTS AND DISCUSSION

One first, rough indication of the stabilizing effect of tannic acid is given in Fig.1, where the TGA curves of the neat polymer and of the PHB/TA15 are shown. The effect of TA is apparent from the shift of the weight loss curve to higher temperatures.

When looking at the effect of TA in more details, the situation appears to be more complex. First, TA inhibits the crystallization of PHB upon cooling. This is shown in Fig. 2a, where the DSC traces of the first heating/cooling cycle of PHB/TA5, PHB/TA10 and PHB/TA15 are compared to those of the neat polymer. While the melting peak is essentially unchanged, addition of TA makes the the exothermic crystallization peak to disappear. Crystallization takes place only upon re-melting of the compound, as shown in Fig. 2a. A secondary peak at a lower temperature for the PHB/TA15 sample supports the hypothesis that TA somewhat disturbs the crystallization of PHB, giving rise to a less ordered crystalline form.The addition of tannic acid is also beneficial as far as processing is concerned. Neat PHB could not be processed at 180°C, because melting could not be completed over times of the order of one hour. The situation is much improved for the PHB/TA15 compound, as shown in Fig. 3 where the time dependent oscillatory rheology of the two samples is reported. Visual inspection of the samples showed that a homogeneous melt was already formed only for the PHB/TA15 sample after a very short time after loading.

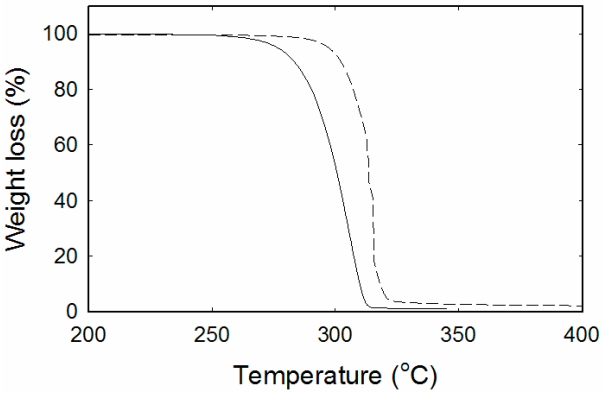

Fig. 1. TGA analysis of the neat PHB (solid line) and of the PHB/TA15 compound

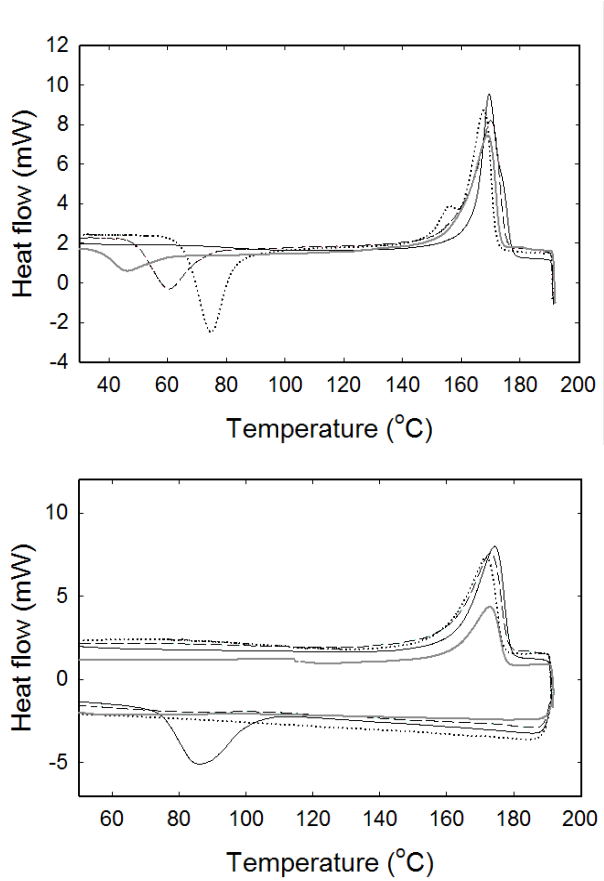

Fig. 2. DSC of neat PHB (solid line), of the PHB/TA10 (broken line) compounds
a) first heating and cooling ramps
b) second heating ramp

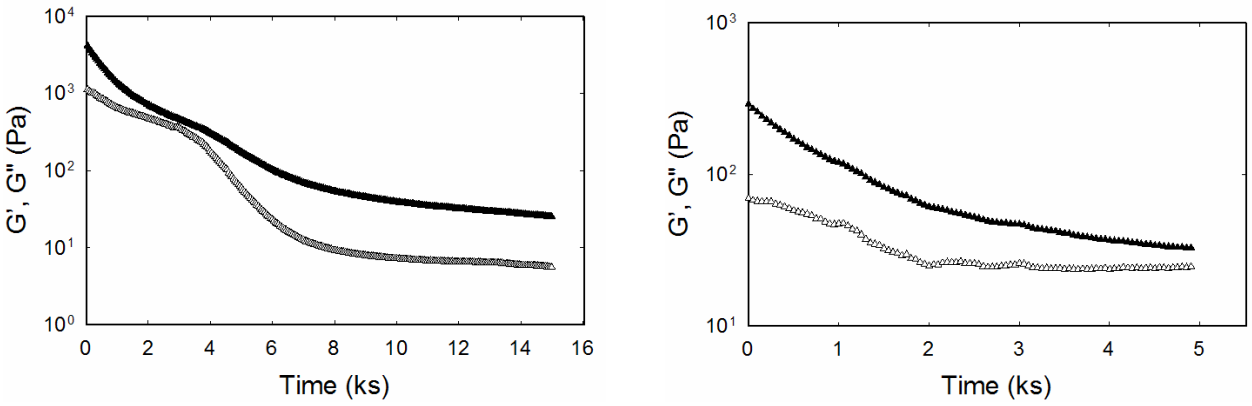

Fig. 3. The time evolution of the elastic (empty symbols) and the loss modulus (filled symbols) at 180°C and a frequency of 10 rad/s.

a) neat polymer *b) PHAB/TA15*

The positive effect of TA on the thermal and rheological stability of PHB is also confirmed at the higher temperature of 200°C, as shown in Fig. 4. The addition of tannic acid determines higher viscoelastic properties but, most of all, clearly delays the thermal degradation process to longer times.

The rheological analysis of PHB/TA compounds has been complemented with the DSC measurements upon three heating/cooling cycles. Samples were taken out of the rheometer at different test times, and thermograms similar to those already shown in Fig. 2 were obtained. The results are summarized in Table I in terms of melting and crystallization temperatures along three subsequent heating/cooling cycles. In spite of the long residence time allowed in the rheometer, the stabilizing effect of tannic acid is apparent.

In order to get some insight on the TA stabilization mechanism FTIR spectra of PHB and PHB/TA15 were acquired up to 6000 s during a rheological test at 180°C and are shown in Fig. 5. The neat PHB spectra show the presence of main absorption peaks at 2980 and 2940 cm^{-1} due to the aliphatic backbone, and at 1730 cm^{-1} due to the ester carbonyls stretching. The heat treatment at 180°C does not cause major changes in the spectra, except for the evolution of gaseous water, which is responsible for the overlapped absorption lines at about 3600 and 1500 cm^{-1}. The spectra of PHB/TA15 show additional peaks due to tannic acid, namely at 3440 cm^{-1} (O-H stretching), 1610 cm^{-1} (resonance of the aromatic C=C of TA), and 1515 cm^{-1} (in-plane bending of phenyl C-H bonds)[37]. The superposition of the PHB/TA15 spectra over time shows that thermal treatment causes an increase of hydroxyls and aromatic resonances, suggesting that TA ester bonds can undergo hydrolysis, yielding alcohol and carboxylic acid groups. This effect is paralleled by the partial conversion of PHB ester moieties to carboxylic acids, as indicated by the absorption increase at 1715 cm^{-1}.

Based on FTIR results, a possible reaction scheme is depicted in Fig. 6. The steps in Figure 12 would justify the observed, limited dissolution of the thermally treated compounds in chloroform. Moreover studies on other type of additives [9-11] already demonstrated that PHB is prone to form the types of chemical bonding revealed by FTIR.

Table 1: Melting and crystallization temperatures of the fresh PHB/TA15 compound and of the corresponding sample undergoing oscillatory shear flow at 200°C. All temperatures are in °C.

	1st cycle			2nd cycle			3rd cycle		
	T_{m1}	T_{m2}	T_c[b]	T_{m1}	T_{m2}	T_c[b]	T_{m1}	T_{m2}	T_c
Fresh sample	/	171.9	74.8	167.7	156.2	73.1	163.5	149.4	/
1000 s[a]	/	169.2	71.7	167.0	154.7	69.9	162.6	148.2	/
2500 s[a]	182.3	168.6	74.3	165.7	151.9	72.4	161.8	146.2	/
3500 s[a]	182.8	167.5	77.1	163.5	148.9	75.0	159.3	143.3	/

[a] time elapsed in an oscillatory shear flow experiment at the constant temperature of 190°C
[b] the crystallization temperature is that measured during the heating cycle (see text)

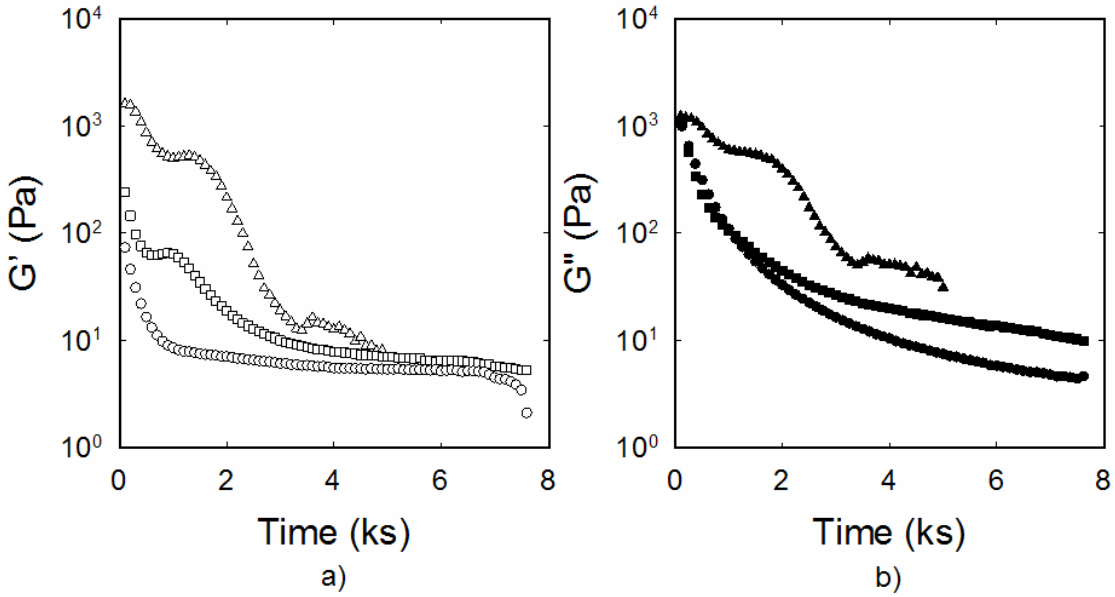

Fig.4. The time evolution of the modulus (a) and the loss modulus (b) at 200°C and a frequency of 10 rad/s: (○, ●) neat PHB; (□, ■) PHB/TA10; (△, ▲) PHB/TA15

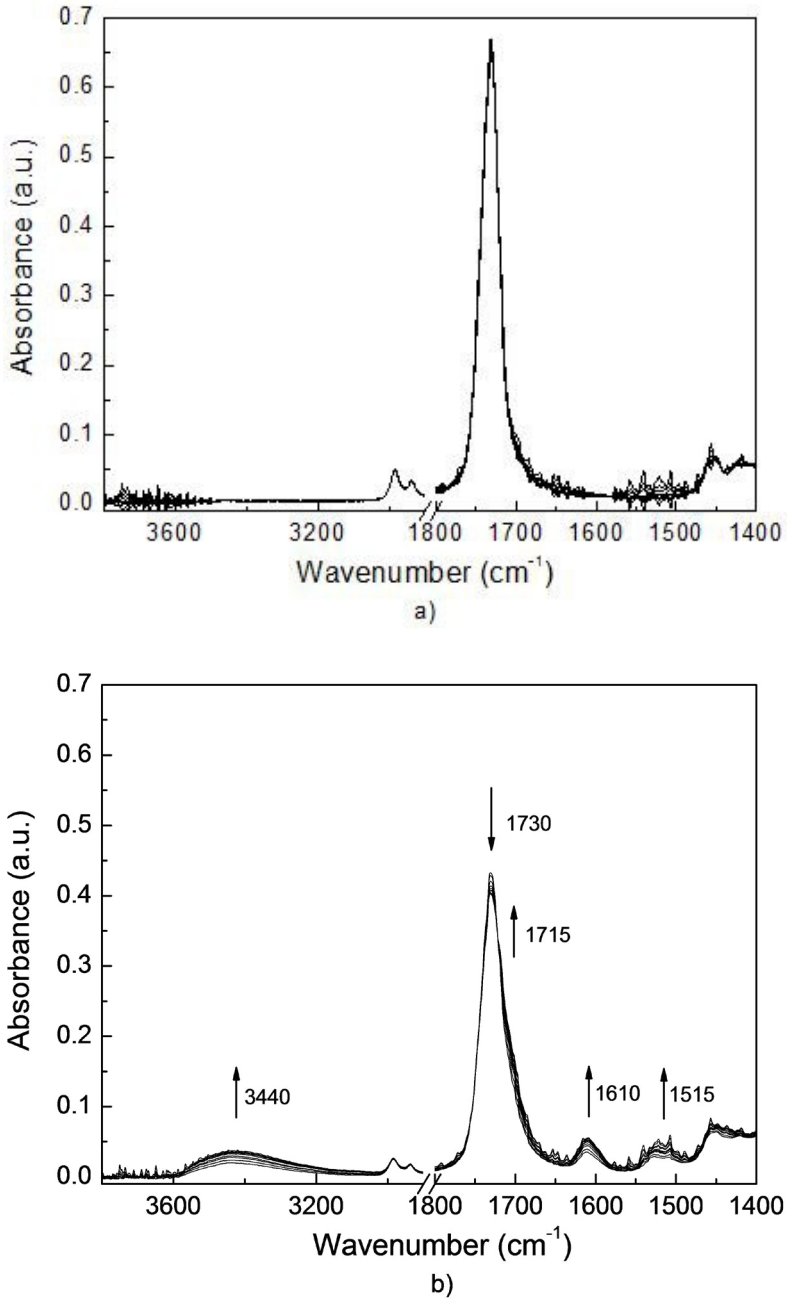

Fig. 5. The time evolution of ATR-FTIR spectra for neat PHB (a) and sample PHB/TA15 (b) up to 6000 s during rheological tests at 180°C

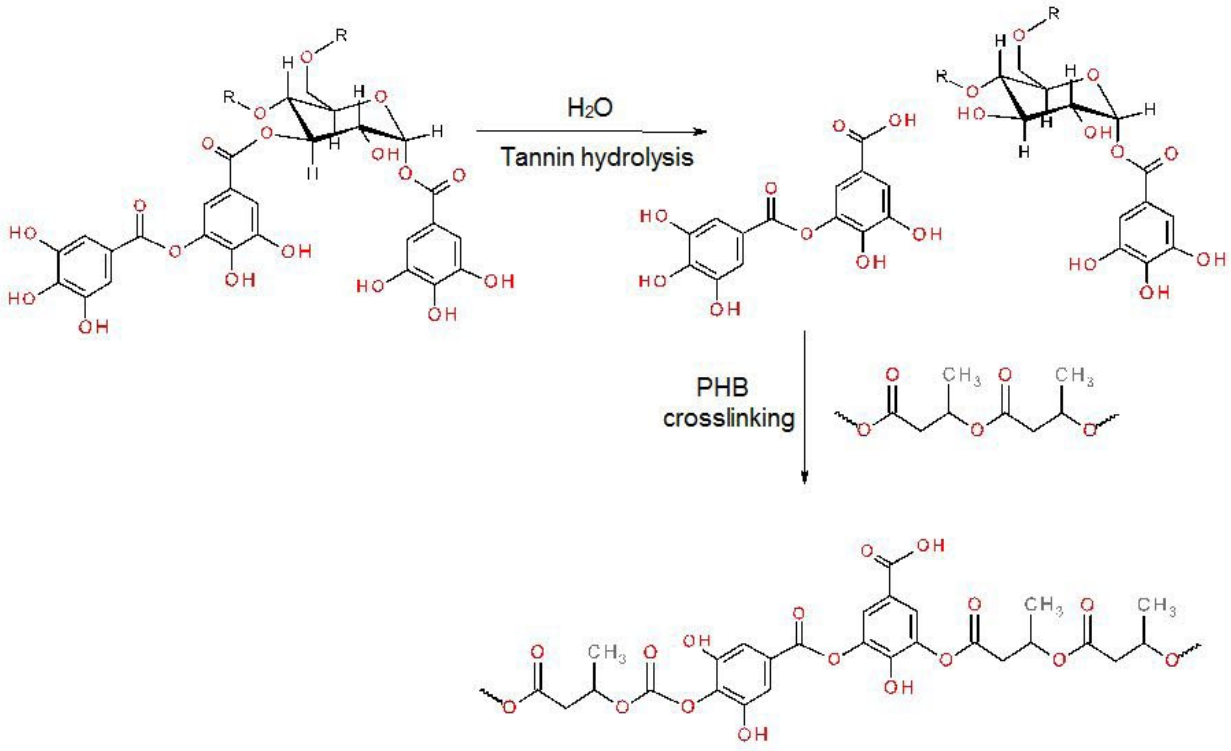

Fig. 6. Tentative mechanism of the crosslinking stabilization of PHB by the tannic acid addition

4.0 CONCLUSIONS

The use of tannic acid, a naturally occurring polyphenol, is found to be effective to improve the thermal stability and processability of PHB, while keeping its biodegradable attitude. Calorimetric and rheological measurements confirm that the neat PHB shows a relatively fast thermal degradation. On the contrary, TA containing samples show a much less pronounced decrease of the viscoelastic moduli over time and the presence of an intermediate, relatively stable region, indicating that thermal degradation is delayed and reduced, a scenario that is confirmed by calorimetry. FTIR measurements support the hypothesis that stabilization is determined by TA/PHB crosslinking.

In conclusion, the results of this study indicate that tannic acid is able to improve the processing properties of PHB both by widening the processability temperature window and by increasing the polymer stability time. As a consequence, lower temperatures and/or longer residence times in the processing equipment are allowed.

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